

CCSF PHYC 4D Lecture Notes

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Chapter 7

The Hydrogen Atom in Wave Mechanics

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Summary of atomic physics

- Chapters 7–9 provide an introduction to atomic and molecular physics.
 - In Chapter 7, we study single electron atoms (atomic hydrogen).
 - In Chapter 8, we generalize to multiple electron atoms.
 - In Chapter 9, we generalize to bound states of multiple atoms (bonded atoms, or molecules).

- The stationary states for a single electron orbiting a nucleus are determined by four quantum numbers: n (principle), l (orbital angular momentum), m_l (magnetic), and m_s (spin). The first three quantum numbers are integers and satisfy

$$n > l \geq 0 \quad -l \leq m_l \leq +l$$

The spin quantum number, m_s , can take on two possible values, $m_s = +\frac{1}{2}$ (spin up) or $m_s = -\frac{1}{2}$ (spin down).

- For each spatial state (determined by n , l , and m_l) there are two spin states. For given values of n and l , there are $2l + 1$ possible values of m_l and $2(2l + 1)$ total possible states. For a given value of n , there are $\sum_{l=0}^{n-1} 2(2l + 1) = 2n^2$ possible states.
- All electron states with the same value of n have the same energy and roughly the same average radius, although the radial probability distribution can be quite different for different values of l . Such electrons are said to occupy the same *shell*. There are $2n^2$ states in a given shell.
- All electron states with the same values of n and l should have the same energy and radial distribution, barring any significant magnetic fields, and are said to occupy the same *subshell*. Such states will have different angular distributions for different values of m_l , but will be indistinguishable in the absence of an external magnetic field. There are $2(2l + 1)$ states in a given subshell.
- The three quantum numbers n , l , and m_l completely determine the spatial distribution of the electron. The two possible spin states share the same spatial wave function. It will be explained later how this is handled mathematically.

- The various shells and subshells can be described using *spectroscopic notation*. The subshells, in order by n and then by l , are:

$$1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, \dots$$

The number to the left is n and the letter represents l using the following code:

$$s = 0 \quad p = 1 \quad d = 2 \quad f = 3 \quad g = 4 \quad \dots$$

- In a multiple electron atom, the single electron states largely retain their identity, and continue to be described by the same set of quantum numbers (n , l , m_l , and m_s), although the states themselves are distorted, both in terms of spatial distribution and energy, due to the presence of the other electrons. It is impossible to determine the wave functions for a multiple electron atom exactly, although computational methods are improving as we speak.
- Each single electron state can be occupied by at most one electron. The electronic state of a multiple electron atom is essentially determined by which single electron states are occupied. The tendency is to fill the lowest energy single electron states first, which usually results in one subshell filling completely before another subshell begins to fill. The electronic structure can be indicated with spectroscopic notation by listing the subshells with the number of electrons in that subshell as a superscript (e.g., oxygen would be $1s^2 2s^2 2p^4$).
- On the basis of the energy levels for the single electron atom, one might expect the order of filling subshells to be:

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, 4d^{10}, 4f^{14}, 5s^2, 5p^6, 5d^{10}, 5f^{14}, 5g^{18}, \dots$$

The superscript in this case represents the maximum capacity of the subshell.

- One might actually have expected no particular ordering of the subshells within a given shell since the energy levels for the hydrogen atom do not depend on l . The fact that higher l values lead to higher energies in multiple electron atoms is based on differences in the radial distribution of the electrons for different values of l and the effects of screening.

- Actually, what *really* happens is that the higher l states are elevated in energy to such an extent that by the time one gets around to filling the $3d$ subshell, the $4s$ subshell has a lower energy. There is a similar reordering between $4d$ and $5s$ and between $4f$ and $6s$. The actual order that subshells are filled is given by

$$\begin{aligned}
 &1s^2 \\
 &2s^2, 2p^6 \\
 &3s^2, 3p^6 \\
 &4s^2, 3d^{10}, 4p^6 \\
 &5s^2, 4d^{10}, 5p^6 \\
 &6s^2, 4f^{14}, 5d^{10}, 6p^6 \\
 &7s^2, 5f^{14}, 6d^{10}, 7p^6 \\
 &\dots
 \end{aligned}$$

At this point, the atoms are too unstable to observe.

- The chemical behavior of each element depends very closely on the electronic structure of the atom, and is well described by the periodic table. The periodic table is in fact organized based on the filling of various subshells (each row in the list above represents a row in the periodic table). This will all be explained in Chapter 8.
- When atoms approach one another, they can bond with one another. A covalent bond results when an electron is being shared between two atoms. This sharing is represented quantum mechanically by replacing the single electron states, which are localized around one atom, with bonding states that represent the electron being shared between the two atoms. If the bonding states have a lower energy than the original states, then bonding will occur.
- Bonding tends to occur only between unpaired electrons in the valence (outermost) shell. In fact, only the s ($l = 0$) and p ($l = 1$) orbitals tend to be involved in bonding, as the higher l states tend to be too deeply buried to participate in bonding (recall that $4s$ is filled before $3d$). There are different types of bonding states depending on whether the single electron states from the two atoms are both s orbitals, both p orbitals, or one is s and the other is p .

- The sharing of electrons between atoms is likely to be unequal if the two atoms are different. In the most extreme case, one atom may steal an electron away from the other atom: no covalent bonding actually occurs. Instead, such a bond is called an *ionic* bond. The two atoms are now ions with opposite charge and attract each other.
- The bonding of a large number of atoms into a macroscopic solid is the subject of Chapter 11 (solid-state physics). In this case, the bonding can either be covalent or ionic bonding between adjacent atoms of the type discussed in Chapter 9, or the bonding can involve electrons being shared by a large number of atoms. Such electrons are said to be *delocalized*, and their wave functions tend to span the entire solid. The different electron states tend to combine into *energy bands*, and many of the properties of a solid (such as its ability to conduct electricity) depend on the details of these energy bands.

Spherical coordinates

- Students should be familiar with spherical coordinates. Fig. 7.8[7.1] (p. 206[208]) of the textbook has a good picture showing how r , θ , and ϕ are defined. Formulas related to spherical coordinates can be found in an appendix at the end of these notes (in-class handout).

Angular momentum

- Consider a particle in three dimensions. At this point, we do not need to assume that this particle is an electron in a hydrogen atom.
- In classical physics, the angular momentum of a particle (relative to the origin) is defined to be $\vec{L} = \vec{r} \times \vec{p}$. In quantum mechanics, the angular momentum is represented by a vector operator

$$\hat{\vec{L}} = \vec{r} \times \hat{\vec{p}} = \frac{\hbar}{i} \vec{r} \times \vec{\nabla}$$

- The x , y , and z components of $\vec{\hat{L}}$ are operators, and are given in both cartesian and spherical coordinates:

$$\begin{aligned}\hat{L}_x &= \frac{\hbar}{i} \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) = \frac{\hbar}{i} \left(-\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_y &= \frac{\hbar}{i} \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) = \frac{\hbar}{i} \left(\cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \\ \hat{L}_z &= \frac{\hbar}{i} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = \frac{\hbar}{i} \frac{\partial}{\partial \phi}\end{aligned}$$

The magnitude-square of the angular momentum operator is given by

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = -\hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right)$$

Note that the angular momentum operator in spherical coordinates operates only on the angular coordinates θ and ϕ . The radial coordinate is not involved.

- States of definite angular momentum can be written in the form

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y_{l, m_l}(\theta, \phi)$$

where $\psi_r(r)$ is an arbitrary radial function and $Y_{l, m_l}(\theta, \phi)$ belongs to a family of angular functions called the *spherical harmonics*.

- The spherical harmonics $Y_{l, m_l}(\theta, \phi)$ are eigenstates of both \hat{L}^2 and L_z :

$$\hat{L}^2 Y_{l, m_l}(\theta, \phi) = l(l+1)\hbar^2 Y_{l, m_l}(\theta, \phi)$$

$$\hat{L}_z Y_{l, m_l}(\theta, \phi) = m_l \hbar Y_{l, m_l}(\theta, \phi)$$

where l and m_l are integers satisfying

$$l \geq 0 \quad -l \leq m_l \leq l$$

In this sense, the spherical harmonics (and hence the complete state $\psi(r, \theta, \phi)$) are states of definite value of both $|\vec{L}|^2$ and L_z .

- The spherical harmonics can be written in the form

$$Y_{l, m_l}(\theta, \phi) = f_{l, m_l}(\theta) e^{im_l \phi}$$

where $f_{l,m_l}(\theta)$ are real-valued polynomial functions of $\cos \theta$ and $\sin \theta$. The spherical harmonics for $l \leq 2$ are given by:

$$\begin{aligned}
Y_{0,0} &= \frac{1}{\sqrt{4\pi}} & Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi} & Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2 \theta e^{\pm 2i\phi} & Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \sin \theta \cos \theta e^{\pm i\phi} \\
Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3 \cos^2 \theta - 1)
\end{aligned}$$

- Note: The fact that the eigenvalues of \hat{L}_z and \hat{L}^2 are quantized is due to the fact that the m_l parameter appearing in the formula for the spherical harmonics must be an integer. This ensures that $e^{im_l\phi} = e^{im_l(\phi+2\pi)}$, which is necessary for $Y_{l,m_l}(\theta, \phi)$ to be continuous. This is related to de Broglie's interpretation of the Bohr hypothesis, in that an integer number of wavelengths must fit in a circle.
- A directional ray from the origin is determined by specifying the two angular coordinates θ and ϕ . A distribution of such rays defines a *solid angle* emanating from the origin. For the range of angular values $[\theta, \theta+d\theta]$ and $[\phi, \phi+d\phi]$, the solid angle is given by

$$d\Omega = \frac{dA}{r^2} = \frac{(r d\theta)(r \sin \theta d\phi)}{r^2} = \sin \theta d\theta d\phi$$

where dA represents the area of the portion of a sphere of radius r intercepted by the solid angle.

- By convention, the spherical harmonics are normalized as follows:

$$\oint_{\text{sph}} |Y_{l,m_l}(\theta, \phi)|^2 d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta |Y_{l,m_l}(\theta, \phi)|^2 = 1$$

The normalized spherical harmonics define the angular probability distribution of the state:

$$P(\theta, \phi) d\Omega = |Y_{l,m_l}(\theta, \phi)|^2 d\Omega = |f_{l,m_l}(\theta)|^2 d\Omega$$

- Fig. 7.11[7.9] (p. 210[217]) of the textbook has some angular plots of probability densities for $l = 0$ and $l = 1$. Fig. 7.10 (p. 219) of the

2nd edition shows both the radial and angular distributions for various states in the hydrogen atom (unfortunately, this figure is omitted in the 3rd edition). Some general things to note about the angular probability distribution:

- The probability density does not depend on ϕ at all.
- For $l = 0$, the probability density is uniform over all solid angles (independent of both θ and ϕ).
- For larger values of l , the probability density is concentrated in smaller and smaller intervals of θ .
- For larger $|m_l|$, the probability density tends to be largest near the x - y plane ($\theta = \pi/2$).

$$f_{l,\pm l}(\theta) \sim \sin^l \theta$$

- For smaller $|m_l|$, the probability density tends to be largest near the z axis ($\theta = 0$ or $\theta = \pi$)

$$f_{l,0}(\theta) \sim \cos^l \theta$$

- Further insight into the “motion” of a particle in a definite angular momentum state can be obtained by computing the *current density* \vec{J} . In one dimension, recall that the current can be calculated as follows:

$$J(x) = \Re \left(\psi(x)^* \frac{\hat{p}}{m} \psi(x) \right)$$

In three dimensions, we replace the one-dimensional momentum operator with the vector momentum operator and use it to compute the current *density* (current per unit cross-sectional area):

$$\begin{aligned} \vec{J}(\vec{r}) &= \Re \left(\psi(\vec{r})^* \frac{\hat{\vec{p}}}{m} \psi(\vec{r}) \right) \\ &= \Re \left(\psi(\vec{r})^* \frac{\hbar}{mi} \vec{\nabla} \psi(\vec{r}) \right) \\ &= \frac{\hbar |\psi(\vec{r})|^2}{m} \Re \left(\frac{\psi(\vec{r})^* \vec{\nabla} \psi(\vec{r})}{i \psi(\vec{r})^* \psi(\vec{r})} \right) \\ &= \frac{\hbar |\psi(\vec{r})|^2}{m} \Im \left(\frac{\vec{\nabla} \psi(\vec{r})}{\psi(\vec{r})} \right) \end{aligned}$$

- Plugging in the wave function yields:

$$\begin{aligned}
\frac{\vec{\nabla}\psi(\vec{r})}{\psi(\vec{r})} &= \frac{1}{\psi_r(r)/r} \frac{\partial}{\partial r} \left(\frac{\psi_r(r)}{r} \right) \hat{r} + \underbrace{\frac{1}{r} \frac{f'(\theta)}{f(\theta)} \hat{\theta}}_{\text{real}} + \frac{1}{r \sin \theta} m_l i \hat{\phi} \\
&= \text{real} + \frac{r}{\psi_r(r)} \left(-\frac{\psi_r(r)}{r^2} + \frac{\psi'_r(r)}{r} \right) \hat{r} + \frac{m_l i}{r \sin \theta} \hat{\phi} \\
&= \text{real} + \frac{\psi'_r(r)}{\psi_r(r)} \hat{r} + \frac{m_l i}{r \sin \theta} \hat{\phi}
\end{aligned}$$

and so

$$\begin{aligned}
\vec{J}(\vec{r}) &= \frac{\hbar |\psi(\vec{r})|^2}{m} \Im \left(\frac{\vec{\nabla}\psi}{\psi} \right) \\
&= \frac{\hbar |\psi(\vec{r})|^2}{m} \left(\Im \left(\frac{\psi'_r(r)}{\psi_r(r)} \right) \hat{r} + \frac{m_l}{r \sin \theta} \hat{\phi} \right)
\end{aligned}$$

- If we identify $\vec{J} = \rho \vec{v}_g$, where $\rho = |\psi(\vec{r})|^2$ is the probability (or number) density, then the “group velocity” of the particle is given by

$$\vec{v}_g = \frac{\hbar}{m} \Im \left(\frac{\psi'_r(r)}{\psi_r(r)} \right) \hat{r} + \frac{m_l \hbar}{m r \sin \theta} \hat{\phi}$$

The radial component is related to the radial wave function and has nothing to do with angular momentum. The ϕ component is equal to the classical velocity of a particle moving in a circle of radius $r \sin \theta$ with angular momentum $L_z = m_l \hbar$. Note that there is no θ component. This will be explained later.

- If the spherical harmonics define states of definite angular momentum, then logically we should be able to determine \vec{L} for a given function $Y_{l,m_l}(\theta, \phi)$. Indeed, $|\vec{L}|^2$ and L_z is determined from the quantum numbers:

$$|\vec{L}|^2 = L_x^2 + L_y^2 + L_z^2 = l(l+1)\hbar^2 \quad L_z = m_l \hbar$$

What about L_x and L_y ? What values do they have in this state? We can calculate

$$\sqrt{L_x^2 + L_y^2} = \sqrt{L^2 - L_z^2} = \sqrt{l(l+1) - m_l^2} \hbar$$

However, it is impossible to determine L_x and L_y separately. They can take any values that satisfy the above relationship. Fig. 7.4[7.8] (p. 202[217]) of the textbook shows the cone of allowed angular momentum vectors \vec{L} .

- It turns out that only one component of \vec{L} can be measured at a time. There is an uncertainty principle relating the different components of \vec{L} that forbid us from being able to determine all of the components at once, unless it happens that $|\vec{L}| = 0$ ($l = 0$).
- So what is special about L_z that allows us to measure that component and not the others? Actually, nothing. It is possible to find states of definite value of L_x or L_y (not both at once!) instead of L_z . In fact, for any given unit vector \hat{n} , it is possible to find states of definite value of $\hat{n} \cdot \vec{L}$. Simply find the eigenstates of the operator

$$\hat{n} \cdot \hat{L} = \hat{n}_x \hat{L}_x + \hat{n}_y \hat{L}_y + \hat{n}_z \hat{L}_z$$

Those eigenstates are in fact linear combinations of Y_{l,m_l} , and involve the same set of eigenvalues: $m'_l \hbar$ where $-l \leq m'_l \leq l$. The reason we picked eigenstates of \hat{L}_z is because the z axis plays a special role in spherical coordinates (consider how simple the operator \hat{L}_z is in spherical coordinates). The resulting wave functions are relatively simple.

- It should be noted that for states that have a definite value of L_z , $\langle L_x \rangle$ and $\langle L_y \rangle$ are both zero. In fact,

$$\langle \hat{n} \cdot \hat{L} \rangle = \hat{n}_z m_l \hbar$$

which is zero whenever \hat{n} is perpendicular to the z axis.

- This can be used to explain why L_x and L_y do not contribute to the current density, and why $J_\theta = 0$ for an angular momentum state quantized along the z axis. Are there rotations around the x and y axes? Yes, because $\sqrt{L_x^2 + L_y^2} > 0$ (unless $l = m_l = 0$). But the wave function is a superposition of different states of definite L_x or L_y , and so in some sense, J_θ should reflect the “average” motion of the particle around those axes. Since $\langle L_x \rangle = \langle L_y \rangle = 0$, there isn’t any.

- Actually, the quantization of angular momentum components in all directions might strike one as a bit puzzling. In fact, if one considers $l = m_l = 3$, one finds that

$$\sqrt{L_x^2 + L_y^2} = \sqrt{3(3+1) - 3^2} \hbar = \sqrt{3} \hbar$$

There is no combination of integers m_x and m_y that can result in

$$\sqrt{L_x^2 + L_y^2} = \sqrt{m_x^2 + m_y^2} \hbar = \sqrt{3} \hbar$$

- One can go beyond this and imagine that components of \vec{L} along *every* axis is simultaneously an integral multiple of \hbar . The fallacy of this objection is in the word “simultaneous”. Since one cannot measure two different components of \vec{L} simultaneously, it doesn’t make sense to think of \vec{L} as somehow quantized in two different directions simultaneously. As we just showed, this leads to absurdity.
- What *is* true, however, is that if one were to prepare a given particle in a definite angular momentum state around some fixed axis and then make a measurement of the component of \vec{L} along a *different* direction, the result of *that* measurement will be an integral multiple of \hbar . In the process of making that measurement, the state of the particle will switch to a definite angular momentum state along the new axis. Any other subsequent measurements of components of \vec{L} along any axes will likewise continue to give integral multiples of \hbar . Measurement along each subsequent axis, however, will destroy the quantization along any previous axis. The Stern-Gerlach experiment (discussed later) can be used to demonstrate this fact experimentally. In fact, I suspect the original Stern-Gerlach experiment included this test (I need to check references to make sure).

Spherical potentials

- According to classical physics, a spherical potential energy function $U(r)$ (i.e., one that depends only on r and not θ or ϕ) implies a central force:

$$\vec{F}(r) = -U'(r) \hat{r}$$

which exerts zero torque relative to the origin. As a consequence, the angular momentum of the particle is conserved.

- Quantum mechanics produces a similar result: a spherical potential energy function $U(r)$ leads to stationary states that are states of *definite angular momentum*, of the type we have just described. Since the states are *stationary* states, this definite value of angular momentum will persist forever. It is in this sense that angular momentum is conserved in quantum mechanics.
- A similar result occurs with linear momentum for a free particle. In classical physics, a free particle experiences no force and so its linear momentum remains constant. In quantum mechanics, the stationary states of the free particle are states of definite momentum.
- It should also be noted that in quantum mechanics, there is a deep connection between symmetries of the universe and conserved quantities. This connection would be revealed by a more advanced treatment of quantum mechanics that makes heavier use of operators.
- The time-independent Schrodinger Equation with a spherical potential energy function takes the form:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + U(r)\psi(\vec{r}) = E\psi(\vec{r})$$

To take advantage of the spherical symmetry, we employ spherical coordinates.

- The Laplacian of the wave function in spherical coordinates is given by

$$\begin{aligned}\nabla^2\psi &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \\ &= \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{1}{r^2} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} \right) \\ &= \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) - \frac{\hat{L}^2 \psi}{\hbar^2 r^2}\end{aligned}$$

- Plugging this into the Schrodinger equation yields

$$-\frac{\hbar^2}{2m} \frac{1}{r} \frac{\partial^2}{\partial r^2} (r\psi) + \frac{\hat{L}^2 \psi}{2mr^2} + U(r)\psi(\vec{r}) = E\psi(\vec{r})$$

- We now separate the wave function into radial and angular functions:

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y(\theta, \phi)$$

At this point, we have not yet established that these are states of definite angular momentum, so we have not labeled $Y(\theta, \phi)$ with the angular momentum quantum numbers.

- Substituting this back into the Schrodinger equation yields:

$$-\frac{\hbar^2}{2m} \frac{\psi_r''(r)}{r} Y(\theta, \phi) + \frac{\psi_r(r)}{r} \frac{\hat{L}^2 Y(\theta, \phi)}{2mr^2} + U(r) \frac{\psi_r(r)}{r} Y(\theta, \phi) = E \frac{\psi_r(r)}{r} Y(\theta, \phi)$$

Now divide out $\psi(r, \theta, \phi)$ to get

$$-\frac{\hbar^2}{2m} \frac{\psi_r''(r)}{\psi_r(r)} + \frac{1}{2mr^2} \frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi)} + U(r) = E$$

- The only part of this equation that depends on θ and ϕ is the combination $\hat{L}^2 Y/Y$. If we fix the value of r and allow θ and ϕ to vary, we realize that $\hat{L}^2 Y/Y$ must be a constant, and so

$$\hat{L}^2 Y(\theta, \phi) = \alpha Y(\theta, \phi)$$

The solutions to this differential equation are the spherical harmonics $Y_{l,m_l}(\theta, \phi)$ and the eigenvalue α is $l(l+1)\hbar^2$.

- It follows that the stationary states are states of definite angular momentum

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y_{l,m_l}(\theta, \phi)$$

where

$$\hat{L}^2 Y_{l,m_l} = l(l+1)\hbar^2 Y_{l,m_l} \quad \hat{L}_z Y_{l,m_l} = m_l \hbar Y_{l,m_l}$$

and l and m_l are integers with $l \geq 0$ and $-l \leq m_l \leq l$.

- Substituting this back into the Schrodinger equation (multiplying through by $\psi_r(r)$ again) yields the *radial equation*:

$$-\frac{\hbar^2}{2m} \psi_r''(r) + \left(\frac{l(l+1)\hbar^2}{2mr^2} + U(r) \right) \psi_r(r) = E \psi_r(r)$$

The term in parentheses:

$$U_{\text{eff}}(r) = \frac{l(l+1)\hbar^2}{2mr^2} + U(r)$$

is sometimes called the *effective potential energy*. It takes into account centrifugal effects.

- The probability density is given by

$$\begin{aligned} P(r, \theta, \phi) d^3\vec{r} &= |\psi(r, \theta, \phi)|^2 (dr)(r^2 d\Omega) \\ &= \frac{|\psi_r(r)|^2}{r^2} (r^2 dr) |Y_{l,m_l}(\theta, \phi)|^2 d\Omega \\ &= (|\psi_r(r)|^2 dr) (|Y_{l,m_l}(\theta, \phi)|^2 d\Omega) \end{aligned}$$

The spherical harmonics have been normalized so that

$$\int_{\text{sph}} |Y_{l,m_l}(\theta, \phi)|^2 d\Omega = 1$$

The entire wave function can be normalized by normalizing the radial wave function:

$$\int_0^\infty |\psi_r(r)|^2 dr = 1$$

The probability of finding the particle at a radius between r and $r + dr$ is $|\psi_r(r)|^2 dr$.

- Consider the free particle ($U(r) = 0$). The radial equation becomes

$$-\frac{\hbar^2}{2m}\psi_r''(r) + \frac{l(l+1)\hbar^2}{2mr^2}\psi_r(r) = E\psi_r(r)$$

The general solution to the radial equation can be expressed in terms of spherical Bessel and Neumann functions. For $l = 0$, the solutions are

$$\psi_r(r) = Ae^{\pm ikr} \quad k = \sqrt{\frac{2mE}{\hbar^2}}$$

which yields

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y_{0,0}(\theta, \phi) = \frac{A}{\sqrt{4\pi}} \frac{e^{\pm ikr}}{r}$$

- These solutions represent outgoing (+) or incoming (−) spherical waves centered around the origin, a fact that can be verified by computing the radial component of the current density:

$$J_r = |\psi(\vec{r})|^2 \frac{\hbar}{m} \Im \left(\frac{\psi'_r(r)}{\psi_r(r)} \right) = \pm |\psi(\vec{r})|^2 \frac{\hbar k}{m}$$

- Such waves require a source or sink of particles at the origin. If no such thing exists, a standing wave can be created by superposition. The result is

$$\psi(r, \theta, \phi) = \frac{A}{\sqrt{4\pi}} \frac{\sin(kr)}{r}$$

The alternative solution involving a cosine function diverges at $r = 0$.

- The three-dimensional harmonic oscillator is also represented by a spherical potential energy function $U(r) = \frac{1}{2}m\omega_0^2 r^2$. Stationary states are of the form

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y_{l,m_l}(\theta, \phi)$$

where $\psi_r(r)$ satisfies:

$$-\frac{\hbar^2}{2m} \psi_r''(r) + \left(\frac{\hbar^2 l(l+1)}{2mr^2} + \frac{1}{2}m\omega_0^2 r^2 \right) \psi_r(r) = E \psi_r(r)$$

- Note that the stationary states can also be expressed in the form

$$\psi(x, y, z) = \psi_x(x) \psi_y(y) \psi_z(z)$$

where each constituent wave function is a solution to the one-dimensional harmonic oscillator.

- It should be possible to show that the energy spectrum of the harmonic oscillator is the same whether it is analyzed using cartesian coordinates or spherical coordinates. For any given energy, the angular momentum states should be linear combinations of the corresponding cartesian states, and vice versa.

The hydrogen atom wave functions

- For the hydrogen atom, the potential energy function for the electron is

$$U(r) = -\frac{e^2}{4\pi\epsilon_0} \frac{1}{r}$$

As with any spherical potential energy function, the stationary states are states of definite angular momentum:

$$\psi(r, \theta, \phi) = \frac{\psi_r(r)}{r} Y_{l, m_l}(\theta, \phi)$$

where $\psi_r(r)$ satisfies:

$$-\frac{\hbar^2}{2m} \psi_r''(r) + \left(\frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2}{4\pi\epsilon_0 r} \right) \psi_r(r) = E \psi_r(r)$$

- The radial equation can be simplified by performing a dimensional analysis, similar to what was done for the harmonic oscillator. To that end, we write

$$r = a_0 \eta \quad E = -E_0 \epsilon$$

where η and ϵ are dimensionless parameters and a_0 and E_0 define the standard length and energy scales. If we substitute that into the radial equation and treat ψ_r now as a function of η , we get:

$$-\frac{\hbar^2}{2ma_0^2} \psi_r''(\eta) + \left(\frac{l(l+1)\hbar^2}{2ma_0^2 \eta^2} - \frac{e^2}{4\pi\epsilon_0 a_0 \eta} \right) \psi_r(\eta) = -E_0 \epsilon \psi_r(\eta)$$

Again, $\psi_r(\eta)$ and $\psi_r''(\eta)$ have the same units, and so the coefficients of all of the terms must have the same units. It follows that

$$\frac{\hbar^2}{2ma_0^2} \propto \frac{e^2}{4\pi\epsilon_0 a_0} \propto E_0$$

- Setting the first two terms proportional to each other and solving for a_0 yields

$$a_0 \propto \frac{4\pi\epsilon_0 \hbar^2}{2me^2}$$

The proportionality constant is chosen arbitrarily by dropping the factor of 2. The result is

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

which turns out to be the Bohr radius.

- Evaluating the first two coefficients:

$$\frac{\hbar^2}{2ma_0^2} = \frac{\hbar^2}{2m} \frac{m^2 e^4}{(4\pi\epsilon_0)^2 \hbar^4} = \frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} = E_0$$

$$\frac{e^2}{4\pi\epsilon_0 a_0} = \frac{e^2}{4\pi\epsilon_0} \frac{me^2}{4\pi\epsilon_0 \hbar^2} = \frac{me^4}{(4\pi\epsilon_0)^2 \hbar^2} = 2E_0$$

Both of these terms are indeed proportional to each other, and are also proportional to E_0 . We arbitrarily chose E_0 to be the first coefficient, so that the second coefficient is $2E_0$. According to the Bohr model, the ground state energy of hydrogen is $-E_0$.

- If we substitute all of this back into the radial equation and divide out E_0 , we get the dimensionless radial equation:

$$-\psi_r''(\eta) + \left(\frac{l(l+1)}{\eta^2} - \frac{2}{\eta} \right) \psi_r(\eta) = -\epsilon \psi_r(\eta)$$

- The complete solution to this differential equation is similar to the harmonic oscillator, only considerably more involved. The end result, however, is not that complicated. The allowed values of ϵ and the corresponding radial wave functions are given by

$$\psi_r(\eta) = a_0^{-1/2} f_{n,l}(\eta) \eta^{l+1} e^{-\eta/n} \quad \epsilon = 1/n^2$$

where n is an integer greater than l and

$$f_{n,l}(\eta) = \sum_{k=0}^{n-(l+1)} b_k \eta^k$$

is a polynomial of order $n - (l + 1)$. The coefficients satisfy the following recurrence relation:

$$b_{k+1} = \frac{2}{n} \frac{k + l + 1 - n}{(k + 1)(k + 2l + 2)} b_k$$

The coefficient b_0 is determined by normalization.

- The overall wave function can now be written

$$\psi_{n,l,m_l}(r, \theta, \phi) = a_0^{-3/2} \left(\sum_{k=l}^{n-1} b_{k-l} (r/a_0)^k \right) e^{-r/na_0} Y_{l,m_l}(\theta, \phi) \quad E_n = -E_0/n^2$$

The quantum numbers n , l , and m_l are all integers and satisfy

$$n > l \geq 0 \quad -l \leq m_l \leq l$$

- The first few wave functions are given by:

$$\begin{aligned}
\psi_{1s}(r, \theta, \phi) &= a_0^{-3/2} 2 e^{-r/a_0} Y_{0,0}(\theta, \phi) \\
\psi_{2s}(r, \theta, \phi) &= a_0^{-3/2} \frac{1}{\sqrt{2}} (1 - \frac{1}{2}(r/a_0)) e^{-r/2a_0} Y_{0,0}(\theta, \phi) \\
\psi_{2p}(r, \theta, \phi) &= a_0^{-3/2} \frac{1}{2\sqrt{6}} (r/a_0) e^{-r/2a_0} Y_{1,m_l}(\theta, \phi) \\
\psi_{3s}(r, \theta, \phi) &= a_0^{-3/2} \frac{2}{3\sqrt{3}} (1 - \frac{2}{3}(r/a_0) + \frac{2}{27}(r/a_0)^2) e^{-r/3a_0} Y_{0,0}(\theta, \phi) \\
\psi_{3p}(r, \theta, \phi) &= a_0^{-3/2} \frac{4\sqrt{2}}{27\sqrt{3}} ((r/a_0) - \frac{1}{6}(r/a_0)^2) e^{-r/3a_0} Y_{1,m_l}(\theta, \phi) \\
\psi_{3d}(r, \theta, \phi) &= a_0^{-3/2} \frac{2\sqrt{2}}{81\sqrt{15}} (r/a_0)^2 e^{-r/3a_0} Y_{2,m_l}(\theta, \phi)
\end{aligned}$$

Probability distributions

- The angular probability distributions for the spherical harmonics were discussed earlier. That discussion applies equally well to the hydrogen atom as it does to any spherical potential energy function. The radial probability distribution for each stationary state depends on the radial wave function, and is unique to each potential energy function $U(r)$.
- As a reminder, the radial probability density is given by

$$P(r) dr = |\psi_r(r)|^2 dr$$

This represents the probability that the particle is located at a radius between r and $r + dr$. The radial wave function is normalized so that

$$\int_0^\infty |\psi_r(r)|^2 dr = 1$$

Expectation values of arbitrary functions of r can be calculated from these normalized wave functions:

$$\langle g(r) \rangle = \int_0^\infty g(r) |\psi_r(r)|^2 dr$$

- For the hydrogen atom, the normalization integral can be expressed in terms of the dimensionless parameter η :

$$1 = \int_0^\infty |\psi_r(\eta)|^2 a_0 d\eta = \int_0^\infty |f_{n,l}(\eta)|^2 \eta^{2l+2} e^{-2\eta/n} d\eta$$

The coefficient b_0 is determined by this condition, with the help of the following integral

$$\int_0^\infty x^k e^{-\alpha x} dx = k!/\alpha^{k+1}$$

$\langle r \rangle$ and $\langle r^2 \rangle$ (which is used to calculate δr) can likewise be computed in terms of the dimensionless parameter:

$$\begin{aligned}\langle r \rangle &= a_0^2 \int_0^\infty \eta |\psi_r(\eta)|^2 d\eta \\ &= a_0 \int_0^\infty |f_{n,l}(\eta)|^2 \eta^{2l+3} e^{-2\eta/n} d\eta \\ \langle r^2 \rangle &= a_0^2 \int_0^\infty |f_{n,l}(\eta)|^2 \eta^{2l+4} e^{-2\eta/n} d\eta\end{aligned}$$

- The radial distributions for all states with $n \leq 6$ were evaluated using a computer. The result:

state	$\langle r \rangle$	δr	state	$\langle r \rangle$	δr
1s	$1.5a_0$	$0.866a_0$	5s	$37.5a_0$	$12.990a_0$
2s	$6.0a_0$	$2.449a_0$	5p	$36.5a_0$	$12.952a_0$
2p	$5.0a_0$	$2.236a_0$	5d	$34.5a_0$	$12.639a_0$
3s	$13.5a_0$	$4.975a_0$	5f	$31.5a_0$	$11.522a_0$
3p	$12.5a_0$	$4.873a_0$	5g	$27.5a_0$	$8.292a_0$
3d	$10.5a_0$	$3.969a_0$	6s	$54.0a_0$	$18.493a_0$
4s	$24.0a_0$	$8.485a_0$	6p	$53.0a_0$	$18.466a_0$
4p	$23.0a_0$	$8.426a_0$	6d	$51.0a_0$	$18.248a_0$
4d	$21.0a_0$	$7.937a_0$	6f	$48.0a_0$	$17.493a_0$
4f	$18.0a_0$	$6.000a_0$	6g	$44.0a_0$	$15.556a_0$
			6h	$39.0a_0$	$10.817a_0$

- Some general trends:
 - The average r lies between 1 and 1.5 times $n^2 a_0$, which is the radius predicted by Bohr for the n^{th} orbit.
 - This average decreases slightly for increasing values of l , but it is clear that $\langle r \rangle$ depends more strongly on n than on l .
 - The standard deviation δr also decreases with increasing l .
- It appears that the radial distribution for a given value of n and different values of l have roughly the same average radius, but that the

distribution of r values is narrower for increasing l . In other words, the electron is less likely to be very close or very far away from the nucleus, as compared to $\langle r \rangle$, for the higher l states.

- This is consistent with the radial probability distribution. It is clear that $P(r) \sim r^{2l+2}$ for small r , which leads to an ever decreasing probability of finding the electron around $r = 0$ as l is increased. This actually makes sense, larger angular momentum implies large centrifugal effects, and thus large kinetic energies required when the electron approaches the origin.
- Another thing to note about the radial distributions is that the number of nodes in the radial probability density is equal to the degree of the polynomial $f_{n,l}(\eta)$, which is $n - (l + 1)$. This actually makes sense: for a fixed value of l , $n = l + 1$ represents the lowest energy state (the “ground state”) and has zero intermediate nodes. Each subsequent value of n increases the number of nodes by one.

Spin

- So far, we have discussed one form of angular momentum, called *orbital* angular momentum, which an electron can possess by virtue of its *orbit* around a nucleus. It turns out there is another kind of angular momentum, called *intrinsic spin* (or just spin), which an electron has just by virtue of being an electron.
- Just like orbital angular momentum, spin can be represented by a vector operator $\hat{\vec{S}}$. An electron state of definite spin satisfies

$$\hat{S}^2\psi = s(s+1)\hbar^2\psi \quad \hat{S}_z\psi = m_s\hbar\psi$$

As before, there is nothing special about the z -axis.

- For a given value of s , there are $2s + 1$ spin states, corresponding to $2s + 1$ possible values of m_s ranging from $-s$ to $+s$ and separated by integer values.
- Now for the surprise: for electrons, $s = \frac{1}{2}$, and the two allowed values of m_s are $m_s = +\frac{1}{2}$ (“spin up”) and $m_s = -\frac{1}{2}$ (“spin down”).

- Spin was first discovered by the Stern-Gerlach experiment (1921), in which angular momentum states with different values of m_l were separated by passing the beam through a non-uniform magnetic field. The number of beams expected is equal to $2l + 1$, which should be an odd number. When the experiment was performed with silver atoms, two beams were observed. Ultimately this result was explained by noting that the electrons in the silver atom have a net *orbital* angular momentum of zero, but that the lone 5s electron has spin $\frac{1}{2}$.
- It turns out that other particles also have intrinsic spin. Electrons, protons and neutrons all have spin $\frac{1}{2}$. By contrast, the photon has spin 1.
- The spin of the electron is not derived from the spatial part of its wave function, but instead is independent of it. The complete electron state is described by the product of a spatial wave function and the spin state:

$$\psi = \psi(\vec{r})\chi$$

The spin operators \hat{S}_x , \hat{S}_y , and \hat{S}_z operate on the spin state χ .

- For spin $\frac{1}{2}$ particles, there are two possible spin states χ_{\pm} , characterized by

$$\begin{aligned}\hat{S}^2\chi_+ &= \frac{1}{2}(\frac{1}{2} + 1)\hbar^2\chi_+ & \hat{S}_z\chi_+ &= +\frac{1}{2}\hbar\chi_+ \\ \hat{S}^2\chi_- &= \frac{1}{2}(\frac{1}{2} + 1)\hbar^2\chi_- & \hat{S}_z\chi_- &= -\frac{1}{2}\hbar\chi_-\end{aligned}$$

- The spin states are represented by 2×1 “column vectors”

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

A general spin state is a linear combination of these two spin states, and is given by

$$\begin{pmatrix} c_+ \\ c_- \end{pmatrix} = c_+\chi_+ + c_-\chi_-$$

- The spin operators are given by 2×2 matrices:

$$\hat{S}_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \hat{S}_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \hat{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

It is a simple matter of matrix multiplication to check that

$$\hat{S}^2 \chi_{\pm} = (\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2) \chi_{\pm} = \frac{3}{4} \hbar^2 \chi_{\pm} \quad \hat{S}_z \chi_{\pm} = \pm \frac{1}{2} \hbar \chi_{\pm}$$

with this representation.

- The representation for higher spins is similar, and involves vectors and matrices with more components.
- The complete state for a spin up or spin down electron is given by

$$\psi_+ = \psi_+(\vec{r}) \chi_+ = \begin{pmatrix} \psi_+(\vec{r}) \\ 0 \end{pmatrix} \quad \psi_- = \psi_-(\vec{r}) \chi_- = \begin{pmatrix} 0 \\ \psi_-(\vec{r}) \end{pmatrix}$$

The most general electron state is given by

$$\psi = \begin{pmatrix} \psi_+(\vec{r}) \\ \psi_-(\vec{r}) \end{pmatrix} = \psi_+(\vec{r}) \chi_+ + \psi_-(\vec{r}) \chi_-$$

The probability of finding the electron in the spin up/down state in a small volume $d^3\vec{r}$ around \vec{r} is given by

$$P_+(\vec{r}) d^3\vec{r} = |\psi_+(\vec{r})|^2 d^3\vec{r} \quad P_-(\vec{r}) d^3\vec{r} = |\psi_-(\vec{r})|^2 d^3\vec{r}$$

The probability of finding the electron in a small volume $d^3\vec{r}$ around \vec{r} *regardless* of its spin state is

$$P(\vec{r}) d^3\vec{r} = (|\psi_+(\vec{r})|^2 + |\psi_-(\vec{r})|^2) d^3\vec{r}$$

The probability of finding the electron in a spin up/down state regardless of position is

$$P_+ = \iiint_{\text{spc}} |\psi_+(\vec{r})|^2 d^3\vec{r} \quad P_- = \iiint_{\text{spc}} |\psi_-(\vec{r})|^2 d^3\vec{r}$$

Normalization requires

$$\iiint_{\text{spc}} (|\psi_+(\vec{r})|^2 + |\psi_-(\vec{r})|^2) d^3\vec{r} = P_+ + P_- = 1$$

Magnetic interactions

- For the moment, we will ignore the electron's intrinsic spin.

- An electron, by virtue of the fact that it has angular momentum, also has a magnetic dipole moment. If we assume that the electron orbits a nucleus in a circular orbit, one can show that

$$\vec{\mu}_L = -\frac{e}{2m}\vec{L}$$

It is remarkable that the quantum mechanical calculation yields the same relationship.

- Thus, an electron in a state (n, l, m_l) has a magnetic dipole moment z component due to its orbital angular momentum given by

$$\mu_{L,z} = -\frac{e\hbar}{2m}m_l = -m_l\mu_B$$

where $\mu_B = e\hbar/(2m) = 9.274 \times 10^{-24}$ J/T is called the Bohr magneton. Technically, $\mu_{L,x}$ and $\mu_{L,y}$ are not zero, but they cannot be measured simultaneously with $\mu_{L,z}$, and their expectation values are zero when the electron is in a state of definite L_z .

- A magnetic dipole $\vec{\mu}$ in a magnetic field \vec{B} has a potential energy $U = -\vec{\mu} \cdot \vec{B}$ and will experience a force $\vec{F} = -\vec{\nabla}U = +\vec{\nabla}(\vec{\mu} \cdot \vec{B})$ if the field is non-uniform.
- If the magnetic field is in the z direction, then the states (n, l, m_l) shift in energy by an amount

$$\Delta E = -\vec{\mu} \cdot \vec{B} = -\mu_{L,z}B_z = +m_l\mu_B B_z$$

We are making a first-order approximation and assuming that the states themselves are unaffected by the presence of the field. This energy shift depends on m_l , and so the states represented by the same n (and l in a multi-electron atom) but different m_l no longer have the same energy. The presence of the magnetic field breaks the energy level degeneracy and, in effect, measures L_z .

- If the field is *not* in the z direction, then the states (n, l, m_l) (characterized by definite values of L_z) are no longer stationary states. It is appropriate in this case to consider states of definite $\hat{n} \cdot \vec{L}$, where \hat{n} is parallel to \vec{B} . Normally, we just rotate the coordinate system so that \vec{B} points in the z direction. It should be noted in any case that placing an

atom in a magnetic field \vec{B} effectively measures the angular momentum component in the direction of \vec{B} .

- The Stern-Gerlach experiment (1921) was designed to demonstrate the quantization of angular momentum components. In this experiment, a beam of atoms is passed through a non-uniform magnetic field (in, say, the z direction). An atom in a given state (n, l, m_l) will experience a force

$$\vec{F} = \vec{\nabla}(\vec{\mu} \cdot \vec{B}) = -m_l \mu_B \vec{\nabla} B_z$$

while it is in the field. Atoms with different values of m_l will deflect differently, causing the beam to split into $2l + 1$ distinct beams. When this experiment was conducted with silver atoms, two beams resulted, which implies $l = \frac{1}{2}$. This ultimately led to the discovery of electron spin.

- The Stern-Gerlach experiment can also be used to demonstrate that measuring one component of angular momentum effectively destroys the previous measurement of any other component. For example, suppose a beam of silver atoms were passed through a magnetic field in the z -direction, splitting the beam into two beams depending on the value of L_z (actually S_z) for the atom. Now pass one of the two beams through another magnetic field in the z -direction, and (no surprise), only one beam comes out, simply confirming the original L_z measurement. However, suppose instead that one of the beams coming from the first magnetic field in the z -direction were passed through a magnetic field in the x -direction (effectively measuring L_x) and then one of the two outgoing beams were passed through a field in the z -direction, re-measuring L_z . In that case, two beams will come out again. The act of measuring L_x destroys the original measurement of L_z .
- It turns out that the electron's spin also contributes to the magnetic dipole moment of the atom. The total dipole moment of an electron is given by

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S$$

where

$$\vec{\mu}_L = -\frac{e}{2m} \vec{L} \quad \vec{\mu}_S = -\frac{e}{m} \vec{S}$$

Yes, the factor of two is missing from the denominator for the spin part of the dipole. It follows that the total z component of the magnetic dipole is given by

$$\mu_z = \mu_{L,z} + \mu_{S,z} = -(m_l + 2m_s)\mu_B$$

The results of the Stern-Gerlach experiment are consistent with $l = 0$ and $s = \frac{1}{2}$, which are the correct quantum numbers for the valence electron of the silver atom.

- The protons and neutrons in the nucleus also contribute to the magnetic dipole moment of an atom, but their contributions are much smaller than the electron because of their large mass. The neutron contributes to the magnetic dipole moment because it is made of charged quarks.
- It turns out that there is an interaction between the spin of an electron and its orbital angular momentum. The source of this interaction actually has to do with the nucleus, and has to do with the fact that in the electron's reference frame, the *nucleus* appears to be orbiting the electron. The resulting magnetic dipole interacts with the electron's spin magnetic dipole, resulting in an energy shift proportional to $+\vec{L} \cdot \vec{S}$. This energy shift is either positive or negative depending on whether \vec{L} is parallel or anti-parallel to \vec{S} . Thus, the two spin states (with different m_s) are now separated in energy.
- The textbook uses the Bohr model to approximate the energy shifts of the two spin states. A more honest calculation found in an advanced quantum textbook yields

$$\delta E = E - E_n = \begin{cases} +|E_n| \frac{1}{(2l+1)(l+1)} \frac{(Z\alpha)^2}{n} & \text{if } \vec{S} \parallel \vec{L} \\ -|E_n| \frac{1}{(2l+1)(l)} \frac{(Z\alpha)^2}{n} & \text{if } \vec{S} \parallel -\vec{L} \end{cases}$$

for a total energy difference of

$$\Delta E = |E_n| \frac{1}{l(l+1)} \frac{(Z\alpha)^2}{n}$$

- Note: There should actually be *no* energy shift for $l = 0$ since $\vec{L} = 0$ in that case. The fact that the formulas above give ∞ probably reflect the fact that the first-order approximation that was performed in the advanced textbook broke down.

Photon emission spectrum

- When the electron makes a transition from a higher energy state E_i to a lower energy state E_f , the atom emits a photon whose energy makes up the difference:

$$\frac{hc}{\lambda} = h\nu = -\Delta E = E_i - E_f$$

Given that $E_n = -E_0/n^2$, this leads to the Rydberg formula for the hydrogen atom emission spectrum:

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

where $R_\infty = E_0/hc$. This formula was determined from experimental data by Rydberg in the 1890's, and successfully explained, first by the Bohr model, and then subsequently with the (more complete) Schrodinger Equation solution to the hydrogen atom.

- A more complete energy level diagram for $n \leq 4$ is given in the textbook (Fig 7.19[7.20], p. 217[225]), depicting the energy levels of the subshells:

$$\begin{array}{ll} -0.8 \text{ eV} & 4s, 4p, 4d, 4f \\ -1.5 \text{ eV} & 3s, 3p, 3d \\ -3.4 \text{ eV} & 2s, 2p \\ -13.6 \text{ eV} & 1s \end{array}$$

- Although it is not evident from the hydrogen atom spectrum, not all energetically allowed transitions actually occur. For example, even though $2s$ is higher energy than $1s$, transitions from $2s$ to $1s$ either do not occur, or else occur very slowly compared to transitions from $2p$ to $1s$ and $3p$ to $2s$ or $1s$. It turns out that photon emission is subject to the following *selection rules*:

$$\Delta l = \pm 1 \quad \Delta m_l = 0, \pm 1$$

This is related to the fact that the photon is a spin 1 particle, and thus carries away one unit of angular momentum.

- The energy spectrum $E_n = -E_0/n^2$ is only strictly true in the absence of magnetic effects. Suppose for the moment that the atom is placed in a magnetic field in the z direction. This results in an energy level shift for a given state (n, l, m_l) of

$$\Delta E = m_l \mu_B B_z$$

- Note that states with different values of m_l will shift by different energies, and so if an electron makes a transition from one state to another with a different value of m_l , then the energy of the photon will either increase or decrease by $\Delta m_l \mu_B B_z$ compared to what it would be without the field. This is known as the Zeeman effect.
- Fig. 7.21[7.22] (p. 218[226]) in the textbook shows the resulting energy split in the $2p$ subshell and the resulting shift in photon energies as the electron transitions to $1s$ (which is *not* split). This will result in one spectral line splitting into three lines, as there are now three possible transitions. The amount of the splitting will depend on B_z . Note: the picture in the textbook is misleading, in that it suggests that a higher ΔE results in a higher emitted wavelength (problem persists in the 3rd edition). This is backwards.
- Note that since $|\Delta m_l| \leq 1$, spectral lines will never split into more than three lines as a result of the Zeeman effect, even if the transition in question is $3d \rightarrow 2p$ (which split into 5 and 3 energy levels, respectively).
- Also note that our analysis of the Zeeman effect ignores the effect of the electron's spin. Taking spin into account complicates the effect. Fig. 7.22[7.23] (p. 219[227]) of the textbook shows experimental data demonstrating what can happen when spin effects are important (the 2nd edition textbook shows the results for Rhodium, 3rd edition shows Zeeman's own results for sodium).
- There is also a split in the spectral lines, known as *fine structure splitting* which results from the spin-orbit interaction discussed earlier. This is also a magnetic effect, but the magnetic field comes from the nucleus, not an external source, and so this split is always present. It is very small, however, and only reveals itself with careful measurement.

Adding angular momentum

- If \vec{J}_1 and \vec{J}_2 are two contributions to the angular momentum of a system, then the total angular momentum is given by $\vec{J} = \vec{J}_1 + \vec{J}_2$. In quantum mechanics, \vec{J}_1 , \vec{J}_2 , and \vec{J} are all represented by operators.
- As an example, the total angular momentum of the electron in an atom would be given by $\vec{J} = \vec{L} + \vec{S}$, the sum of the electron's orbital and spin angular momentum. In a multiple electron atom, the angular momentum of each electron can also be added to give the total angular momentum for the electronic state of the atom.
- The angular momentum state of a system with two angular momentum contributions can be represented in two ways: (1) specifying the angular momenta \vec{J}_1 and \vec{J}_2 separately, and (2) by specifying the total angular momentum \vec{J} (along with some information about \vec{J}_1 and \vec{J}_2). Remember that not all components of \vec{J}_1 , \vec{J}_2 , or \vec{J} can be specified simultaneously because of uncertainty relations.
- The quantum numbers associated with the first representation are j_1 , m_{j1} , j_2 , and m_{j2} . The state satisfies

$$\begin{aligned}\hat{J}_1^2\psi &= j_1(j_1 + 1)\hbar^2\psi & \hat{J}_{1z}\psi &= m_{j1}\hbar\psi \\ \hat{J}_2^2\psi &= j_2(j_2 + 1)\hbar^2\psi & \hat{J}_{2z}\psi &= m_{j2}\hbar\psi\end{aligned}$$

For given values of j_1 and j_2 , there are $(2j_1 + 1)(2j_2 + 1)$ total states.

- The quantum numbers associated with the second representation are j_1 , j_2 , j , and m_j . The state satisfies

$$\begin{aligned}\hat{J}_1^2\psi &= j_1(j_1 + 1)\hbar^2\psi & \hat{J}_2^2\psi &= j_2(j_2 + 1)\hbar^2\psi \\ \hat{J}^2\psi &= j(j + 1)\hbar^2\psi & \hat{J}_z\psi &= m_j\hbar\psi\end{aligned}$$

Note that J_{1z} and J_{2z} are no longer specified separately. Specifying J^2 precludes this.

- Each state in the second representation can be expressed as a linear combination of states in the first representation. For fixed values of j_1 and j_2 , the quantum numbers j and m_j satisfy

$$|j_1 - j_2| \leq j \leq j_1 + j_2 \quad -j \leq m_j \leq j$$

giving a total number of states

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} 2j+1 = (j_1+j_2+1)^2 - (j_1-j_2)^2 = (2j_1+1)(2j_2+1)$$

- For example, a spin $\frac{1}{2}$ electron is in an orbital angular momentum state l . The total angular momentum is given by $\vec{J} = \vec{L} + \vec{S}$. We can either specify its state with the quantum numbers (n, l, m_l, s, m_s) (as we have been doing), or with the quantum numbers (n, l, s, j, m_j) . In this case, since $s = \frac{1}{2}$, we must have $j = l \pm \frac{1}{2}$ (or just $j = \frac{1}{2}$ if $l = 0$). Whether $j = l + \frac{1}{2}$ or $j = l - \frac{1}{2}$ is a matter of whether \vec{L} and \vec{S} are predominately parallel or anti-parallel.
- If more than two angular momenta are to be added (as may be the case with multi-electron atoms), they should be added two at a time.

Appendix: Cartesian coordinates (x, y, z)

- Position vector:

$$\vec{r} = x \hat{x} + y \hat{y} + z \hat{z}$$

- Unit vectors:

$$\hat{x} = \hat{x} \quad \hat{y} = \hat{y} \quad \hat{z} = \hat{z}$$

- Cross product:

$$\hat{x} \times \hat{y} = \hat{z} \quad \hat{y} \times \hat{z} = \hat{x} \quad \hat{z} \times \hat{x} = \hat{y}$$

- Length, area, and volume elements:

$$d\vec{s} = dx \hat{x} + dy \hat{y} + dz \hat{z}$$

$$d\vec{a}_{xy} = dx dy \hat{z} \quad d\vec{a}_{yz} = dy dz \hat{x} \quad d\vec{a}_{zx} = dz dx \hat{y}$$

$$dV = dx dy dz$$

- Vector calculus:

$$\vec{\nabla} \psi = \frac{\partial \psi}{\partial x} \hat{x} + \frac{\partial \psi}{\partial y} \hat{y} + \frac{\partial \psi}{\partial z} \hat{z}$$

$$\vec{\nabla} \cdot \vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}$$

$$\vec{\nabla} \times \vec{v} = \left(\frac{\partial v_z}{\partial y} - \frac{\partial v_y}{\partial z} \right) \hat{x} + \left(\frac{\partial v_x}{\partial z} - \frac{\partial v_z}{\partial x} \right) \hat{y} + \left(\frac{\partial v_y}{\partial x} - \frac{\partial v_x}{\partial y} \right) \hat{z}$$

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

Appendix: Cylindrical coordinates (ρ, ϕ, z)

- Position vector:

$$\vec{r} = \rho(\cos \phi \hat{x} + \sin \phi \hat{y}) + z \hat{z}$$

- Unit vectors:

$$\hat{\rho} = \cos \phi \hat{x} + \sin \phi \hat{y} \quad \hat{\phi} = -\sin \phi \hat{x} + \cos \phi \hat{y} \quad \hat{z} = \hat{z}$$

- Cross product:

$$\hat{\rho} \times \hat{\phi} = \hat{z} \quad \hat{\phi} \times \hat{z} = \hat{\rho} \quad \hat{z} \times \hat{\rho} = \hat{\phi}$$

- Non-zero unit vector derivatives:

$$\frac{\partial \hat{\rho}}{\partial \phi} = \hat{\phi} \quad \frac{\partial \hat{\phi}}{\partial \phi} = -\hat{\rho}$$

- Length, area, and volume elements:

$$\begin{aligned}
d\vec{s} &= d\rho \hat{\rho} + \rho d\phi \hat{\phi} + dz \hat{z} \\
d\vec{a}_{\rho\phi} &= \rho d\rho d\phi \hat{z} & d\vec{a}_{\phi z} &= \rho d\phi dz \hat{\rho} & d\vec{a}_{z\rho} &= dz d\rho \hat{\phi} \\
dV &= \rho d\rho d\phi dz
\end{aligned}$$

- Vector calculus:

$$\begin{aligned}
\vec{\nabla}\psi &= \frac{\partial\psi}{\partial\rho} \hat{\rho} + \frac{1}{\rho} \frac{\partial\psi}{\partial\phi} \hat{\phi} + \frac{\partial\psi}{\partial z} \hat{z} \\
\vec{\nabla} \cdot \vec{v} &= \frac{1}{\rho} \frac{\partial}{\partial\rho}(\rho v_\rho) + \frac{1}{\rho} \frac{\partial v_\phi}{\partial\phi} + \frac{\partial v_z}{\partial z} \\
\vec{\nabla} \times \vec{v} &= \left(\frac{1}{\rho} \frac{\partial v_z}{\partial\phi} - \frac{\partial v_\phi}{\partial z} \right) \hat{\rho} + \left(\frac{\partial v_\rho}{\partial z} - \frac{\partial v_z}{\partial\rho} \right) \hat{\phi} + \frac{1}{\rho} \left(\frac{\partial}{\partial\rho}(\rho v_\phi) - \frac{\partial v_\rho}{\partial\phi} \right) \hat{z} \\
\nabla^2\psi &= \frac{1}{\rho} \frac{\partial}{\partial\rho} \left(\rho \frac{\partial\psi}{\partial\rho} \right) + \frac{1}{\rho^2} \frac{\partial^2\psi}{\partial\phi^2} + \frac{\partial^2\psi}{\partial z^2}
\end{aligned}$$

Appendix: Spherical coordinates (r, θ, ϕ)

- Position vector:

$$\vec{r} = r (\sin \theta (\cos \phi \hat{x} + \sin \phi \hat{y}) + \cos \theta \hat{z}) = r (\sin \theta \hat{\rho} + \cos \theta \hat{z})$$

- Unit vectors:

$$\hat{r} = \sin \theta \hat{\rho} + \cos \theta \hat{z} \quad \hat{\theta} = \cos \theta \hat{\rho} - \sin \theta \hat{z} \quad \hat{\phi} = \hat{\phi}$$

- Cross product:

$$\hat{r} \times \hat{\theta} = \hat{\phi} \quad \hat{\theta} \times \hat{\phi} = \hat{r} \quad \hat{\phi} \times \hat{r} = \hat{\theta}$$

- Non-zero unit vector derivatives:

$$\frac{\partial \hat{r}}{\partial \theta} = \hat{\theta} \quad \frac{\partial \hat{\theta}}{\partial \theta} = -\hat{r} \quad \frac{\partial \hat{r}}{\partial \phi} = \sin \theta \hat{\phi} \quad \frac{\partial \hat{\theta}}{\partial \phi} = \cos \theta \hat{\phi} \quad \frac{\partial \hat{\phi}}{\partial \phi} = -\hat{\rho} = -\sin \theta \hat{r} - \cos \theta \hat{\theta}$$

- Length, area, and volume elements:

$$\begin{aligned}
d\vec{s} &= dr \hat{r} + r d\theta \hat{\theta} + r \sin \theta d\phi \hat{\phi} \\
d\vec{a}_{r\theta} &= r dr d\theta \hat{\phi} & d\vec{a}_{\theta\phi} &= r^2 \sin \theta d\theta d\phi \hat{r} & d\vec{a}_{\phi r} &= r \sin \theta d\phi dr \hat{\theta} \\
dV &= r^2 \sin \theta dr d\theta d\phi
\end{aligned}$$

- Solid angle:

$$d\Omega = \frac{da_{\theta\phi}}{r^2} = \sin\theta \, d\theta \, d\phi \quad d\vec{a}_{\theta\phi} = r^2 \, d\Omega \, \hat{r} \quad dV = r^2 \, dr \, d\Omega$$

- Vector calculus:

$$\begin{aligned} \vec{\nabla}\psi &= \frac{\partial\psi}{\partial r} \hat{r} + \frac{1}{r} \frac{\partial\psi}{\partial\theta} \hat{\theta} + \frac{1}{r \sin\theta} \frac{\partial\psi}{\partial\phi} \hat{\phi} \\ \vec{\nabla} \cdot \vec{v} &= \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 v_r) + \frac{1}{r \sin\theta} \frac{\partial}{\partial\theta}(v_\theta \sin\theta) + \frac{1}{r \sin\theta} \frac{\partial v_\phi}{\partial\phi} \\ \vec{\nabla} \times \vec{v} &= \frac{1}{r \sin\theta} \left(\frac{\partial}{\partial\theta}(v_\phi \sin\theta) - \frac{\partial v_\theta}{\partial\phi} \right) \hat{r} + \frac{1}{r} \left(\frac{1}{\sin\theta} \frac{\partial v_r}{\partial\phi} - \frac{\partial}{\partial r}(r v_\phi) \right) \hat{\theta} \\ &\quad + \frac{1}{r} \left(\frac{\partial}{\partial r}(r v_\theta) - \frac{\partial v_r}{\partial\theta} \right) \hat{\phi} \\ \nabla^2\psi &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial\psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \\ &= \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\psi) + \frac{1}{r^2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right) \end{aligned}$$

Appendix: some useful identities

- Angular momentum operators

$$\begin{aligned} \hat{L} &= \vec{r} \times \hat{p} = \frac{\hbar}{i} \vec{r} \times \vec{\nabla} \\ \hat{L}\psi &= \frac{\hbar}{i} \vec{r} \times \vec{\nabla}\psi = \frac{\hbar}{i} \left(\frac{\partial\psi}{\partial\theta} \hat{\phi} - \frac{1}{\sin\theta} \frac{\partial\psi}{\partial\phi} \hat{\theta} \right) \\ \hat{L}_x &= (y\hat{p}_z - z\hat{p}_y) = \frac{\hbar}{i} \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right) \\ \hat{L}_y &= (z\hat{p}_x - x\hat{p}_z) = \frac{\hbar}{i} \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right) \\ \hat{L}_z &= (x\hat{p}_y - y\hat{p}_x) = \frac{\hbar}{i} \frac{\partial}{\partial\phi} \\ \hat{L}_\pm &= \hat{L}_x \pm i\hat{L}_y = \hbar e^{\pm i\phi} \left(i \cot\theta \frac{\partial}{\partial\phi} \pm \frac{\partial}{\partial\theta} \right) \\ \hat{L} \cdot \vec{v} &= \hat{L}_x v_x + \hat{L}_y v_y + \hat{L}_z v_z \\ &= \frac{\hbar}{i} (\vec{r} \times \vec{\nabla}) \cdot \vec{v} = \frac{\hbar}{i} \vec{r} \cdot (\vec{\nabla} \times \vec{v}) = \frac{\hbar}{i} \frac{1}{\sin\theta} \left(\frac{\partial}{\partial\theta}(v_\phi \sin\theta) - \frac{\partial v_\theta}{\partial\phi} \right) \end{aligned}$$

$$\hat{L}^2\psi = \hat{\vec{L}} \cdot (\hat{\vec{L}}\psi) = -\hbar^2 \left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right)$$

$$\nabla^2\psi = \frac{1}{r} \frac{\partial^2}{\partial r^2}(r\psi) - \frac{\hat{L}^2\psi}{\hbar^2 r^2}$$

- The spherical harmonics, $Y_{l,m_l}(\theta, \phi)$, where l and m_l are integers with $l \geq 0$ and $-l \leq m_l \leq l$, represent the angular momentum states, and are eigenstates of the \hat{L}^2 and \hat{L}_z operators:

$$\hat{L}^2 Y_{l,m_l} = l(l+1)\hbar^2 Y_{l,m_l} \quad \hat{L}_z Y_{l,m_l} = m_l \hbar Y_{l,m_l}$$

They are normalized according to:

$$\oint_{\text{sph}} |Y_{l,m_l}(\theta, \phi)|^2 d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta |Y_{l,m_l}(\theta, \phi)|^2 = 1$$

The “ladder operators” \hat{L}_\pm can be used to generate the spherical harmonics for different values of m_l :

$$\begin{aligned} \hat{L}_+ Y_{l,l} &= \hat{L}_- Y_{l,-l} = 0 \\ \hat{L}_+ Y_{l,m_l} &= \sqrt{l(l+1) - m_l(m_l+1)} Y_{l,m_l+1} \\ \hat{L}_- Y_{l,m_l+1} &= \sqrt{l(l+1) - m_l(m_l+1)} Y_{l,m_l} \quad (-l \leq m_l < l) \end{aligned}$$

The first few spherical harmonics:

$$\begin{aligned} Y_{0,0} &= \frac{1}{\sqrt{4\pi}} & Y_{1,\pm 1} &= \mp \sqrt{\frac{3}{8\pi}} \sin\theta e^{\pm i\phi} & Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \cos\theta \\ Y_{2,\pm 2} &= \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{\pm 2i\phi} & Y_{2,\pm 1} &= \mp \sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{\pm i\phi} \\ Y_{2,0} &= \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1) \end{aligned}$$